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(54) CURABLE COMPOSITION AND ITS USE

(57)Abstract:

PURPOSE: To obtain a curable compsn. which gives a cured item having a surface hardly attracting dust by compounding a specific org. polymer and a polymer of a polyfunctional hydrolyzable silane compd. as the essential components.

CONSTITUTION: This compsn. contains as the essential components an org. polymer having at least one reactive silyl group in the molecule and a polymer of a polyfunctional hydrolyzable silane compd. and is useful as a sealant and a coating agent. The org. polymer favorably is a deriv. of a polymer, such as of a polyether, a polyester, polyisobutylene, polychloroprene, or polybutadiene, a deriv. of a polyether being more favorable and a polyoxypropylene compd. having a reactive silyl group at the molecular end being the most favorable. Pref. examples of the silane compd. are methyltrimethoxysilane and tetramethoxysilane.

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CLAIMS

[Claim(s)]

[Claim 1]An organic polymer (A) which has at least one reactive silyl groups in intramolecular, and a hardenability constituent which uses a polymer (B) of a polyfunctional hydrolytic silane compound as an essential ingredient.

[Claim 2]A sealing agent which consists of a hardenability constituent of claim 1.

[Claim 3]A coating obtained by having applied a hardenability constituent of claim 1 to a substrate, and having stiffened it

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]
[Industrial Application] This invention relates to the coating using the sealing agent and this hardenability constituent which consist of a hardenability constituent in which performance with dust, etc. have been improved, and this hardenability constituent

[0002]

[Description of the Prior Art] Conventionally, the method of using it for a sealing agent, adhesives, etc. using the hardening reaction of the organic polymer which has reactive silyl groups at the end which is known as modified silicone system resin is known well, and is a useful method industrially. The polymer which has such reactive silyl groups is proposed by JP.45-36319,B, JP.46-17553,B, JP.61-18582,B, etc., for example.

[0003]

[Problem(s) to be Solved by the Invention] However, the above-mentioned sealing agent had the problem that dirt, such as dust, adhered to the surface especially easily, when it was used outdoors. Therefore, surface dirt had to be removed by operation of damping with a damp towel etc., and reduction of the maintenance was SUBJECT. This invention provides the coating using the sealing agent and hardenability constituent which consist of a hardenability constituent which can reduce a surface sex with dust, and this hardenability constituent

[0004]

[Means for Solving the Problem] An organic polymer (A) in which this invention has at least one reactive silyl groups in intramolecular. And it is a coating obtained by having applied to a substrate a sealing agent which consists of a hardenability constituent which uses a polymer (B) of a polyfunctional hydrolytic silane compound as an essential ingredient, and this hardenability constituent, and this hardenability constituent, and having stiffened them.

[0005] An organicity polymer which contains at least one reactive silyl groups in intramolecular" (only henceforth "an organic polymer (A)") used in this invention, it is preferred that they are derivatives, such as a polyether system polymer, a polyester system polymer, a polyisobutylene system polymer, a polychloroprene system polymer, and a polybutadiene system polymer, and it is preferred that it is especially a derivative of a polyether system polymer.

[0006] "Polyether which contains at least one reactive silyl groups in intramolecular" (only henceforth "polyether (P)") is proposed by JP.3-47825,A, JP.3-72527,A, JP.3-43449,A, JP.3-79627,A, etc., for example.

[0007] Next, although a manufacturing method of polyether (P) is explained, an organic polymer (A) of this invention is not limited to polyether (P). As for polyether (P), it is preferred under existence of a catalyst that it is a derivative of polyoxalkylene which made alkylene oxide, such as propylene oxide, ethylene oxide, and butylene oxide, react to initiators, such as a hydroxy compound which has at least one hydroxyl group, and was manufactured.

[0008] As a catalyst, an alkaline metal catalyst, a porphyrin complex catalyst, a composite metal cyanide complex catalyst, etc. are mentioned. By using a composite metal cyanide complex catalyst, a value of M_w/M_n is lower than a polyoxalkylene polymer manufactured using the conventional alkaline metal catalyst, and since a polyoxalkylene polymer of hypoviscosity is obtained more in the amount of polymers, it is more desirable.

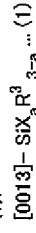
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[0009] As a composite metal cyanide complex, a thing of a statement can be used for JP.46-27250,B. A complex which uses zinchexacyano cobaltate as the main ingredients especially is preferred, and the ether and/or especially an alcoholic complex are preferred. Here, as ether, ethyleneglycol dimethyl ether (glyme), diethylene glycol dimethyl ether (jig lime), etc. are preferred, and glyme is preferred especially from an ease of handling at the time of complex manufacture. As alcohol, t-butanol given in JP.4-145123,A is preferred.

[0010] As for a functional group number of a polyoxalkylene polymer, two or more are preferred, and especially 2-4 are preferred. Specifically, a polyoxyethylene compound, a polyoxypropylene compound, a polyoxy butylene compound, polyoxy hexylene compounds, and/or these copolymers are mentioned.

[0011] They are polyoxypropylene diol, polyoxypropylene triol, and polyoxypropylene tetraol most preferably. When using for a method of the following (b) or (**), a polyoxalkylene polymer of olefin ends, such as an allyl end polyoxypropylene monoar, is also preferred.

[0012] Like a silicon content group which has the hydrolytic basis coupled directly with a silanol group or a silicon atom, reactive silyl groups cause a condensation reaction with hygroscopic surface moisture, a hardening agent, etc., can promote polymers quantification of polyether, and are shown by (1).



However, a hydrolytic basis and a of R^3 are 1, 2, or 3 among a formula (1) substitution of the carbon numbers 1-20 or an unsubstituted univalent hydrocarbon group, and X.

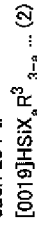
[0014] R^3 in a formula (1) has a with a carbon number of eight or less alkyl group, a phenyl group, or a preferred fluoro alkyl group, and a methyl group, an ethyl group, a propyl group, a propenyl group, a butyl group, a hexyl group, a cyclohexyl group, especially a phenyl group, etc. are preferred.

[0015] As X in a formula (1), a hydroxyl group, a halogen atom, an alkoxy group, an acyloxy group, an amide group, an amino group, an aminoxy group, a KETOKISHI mate group, and a hydride group are illustrated. Among these, as for a carbon number of a hydrolytic basis which has a carbon atom, six or less are preferred, and four especially or less are preferred. Desirable bases are a with a carbon number of four or less lower alkoxy group especially a methoxy group and an ethoxy basis, a propoxy group, a propenyl group, etc.

[0016] As for a in a formula (1), it is preferred that it is especially 2 or 3.

[0017] As for polyether (P), what introduces reactive silyl groups into an end of a polyoxalkylene polymer which has a functional group, and is manufactured is preferred so that it may state to the following (b), (**), and (**). Such a compound is liquefied at a room temperature, and when a hardened material holds pliability and uses for a sealing agent, adhesives, etc. also at low temperature comparatively, it is provided with the desirable characteristic.

[0018] (**) A method to which a silane compound shown by polyoxalkylene polymer which has an olefin group, and a formula (2) is made to react under existence of the 8th group transition metal, such as Pt.

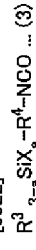


R^3 , X, and a are the same as the above among a formula (2).

[0020] As a method of obtaining a polyoxalkylene polymer which has an olefin group here, A compound which has an olefin group and a functional group is made to react to terminal hydroxyl groups of a polyoxalkylene polymer. When polymerizing a method or alkylene oxide combined by ether bond, ester bond, a urethane bond, carbonate combination, etc., A method of polymerizing alkylene oxide by using as an initiator a compound which has a method or an olefin group, and a hydroxyl group which introduce an olefin group into a side chain, etc. are mentioned by adding and carrying out copolymerization of the olefin group content epoxy compounds, such as allyl glycidyl ether.

[0021] (**) How to make a compound shown by a formula (3) react to an end of a polyoxalkylene polymer which has a hydroxyl group.

[0022]

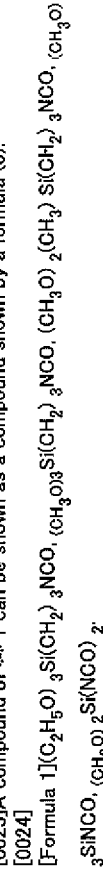


the inside of a formula (3), R^3 , X, and a — the above — the same — R^4 — a divalent hydrocarbon

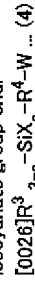
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group of the carbon numbers 1-17.

[0023]A compound of ** 1 can be shown as a compound shown by a formula (3).



[0025](**) A method to which W basis of the silane compound shown in this isocyanate group by a formula (4) is made to react after making polyisocyanate compounds, such as tolylene diisocyanate, react to the end of the polyoxyalkylene polymer which has a hydroxyl group and considering it as an isocyanate group end.



R^3 , R^4 , X, and a are the same as the above among a formula (4). An active hydrogen containing group as which W was chosen from a hydroxyl group, a carboxyl group, a sulfinyl group, and an amino group (the 1st class or the 2nd class).

[0027](**) A method to which an olefin group of a polyoxyalkylene polymer which has the olefin group obtained by a method described above, and a sulfinyl group of a silane compound shown by a formula (4) whose W is a sulfinyl group are made to react.

[0028]As for the number of reactive silyl groups, it is preferred that it is 1.0 or more per molecule in a total molecule average.

[0029]Polymer distribution polyether which a polymer of a polymerization nature unsaturation group content monomer distributes may be sufficient as polyether (P).

[0030]As an organic polymer (A) in this invention, the number average molecular weights 1000-50000, especially an organic polymer of 5000-30000 are preferred. If elongation will become low and a number average molecular weight exceeds 50000 firmly [a hardened material] when a number average molecular weight of an organic polymer (A) is lower than 1000, pliability and elongation of a hardened material are satisfactory, but viscosity of the polymer itself [this] becomes remarkably high, and practicality becomes low. As for especially a number average molecular weight, 8000-30000 are preferred.

[0031]A polyfunctional hydrolytic silane compound is a compound which has the basis which 2-4 hydrolytic bases coupled directly with one silicon atom. "A polymer (B) of a polyfunctional hydrolytic silane compound" (only henceforth "a polymer (B)") many quantifies this compound according to condensation.

[0032]As a hydrolytic basis, an alkoxy group, an alkoxy alkoxy group, an acyloxy group, an aryloxy group, an aminoxy, an amide group, a ketoxime group, an isocyanate group, a halogen atom, etc. are illustrated. It is an alkoxy group preferably and, as for especially the four or less carbon numbers, 1-2 pieces are preferred.

[0033]Functional group numbers of a polyfunctional hydrolytic silane compound are 2-4, and especially 3-4 are preferred. As an example of a desirable polyfunctional hydrolytic silane compound, silane compounds, such as a methyl trimethoxy run, a tetramethoxy silane, ethyltrimethoxysilane, a tetraethoxysilane, vinyltrimethoxysilane, and phenyltriethoxysilane, are mentioned.

[0034]A polymer (B) is a thing of the degree of many quantification which does not generate gel output in a hardenability constituent. Here, the degree of many quantification means condensation molecularity of a polyfunctional hydrolytic silane compound. There is a thing with straight chain shape, a letter of branching, annular, and network structure in a polymer, and it is thought that is the mixture in which what has a letter of branching, annular, and network structure in a thing with a thing which usually has straight-chain-shape structure, or straight-chain-shape structure is contained. A polymer (B) used by this invention may be used as a mixture of what may use a thing with such structures alone, respectively, or has such structures.

[0035]A polymer of tetraalkoxysilane is mentioned as a desirable polymer (B). It is expressed with general formula $\text{RO}(\text{Si}(\text{OR})_2)_n\text{R}$ if this is shown as a thing with straight-chain-shape structure.

[0036]n expresses the degree of many quantification of a polymer among a general formula. Usually, a polymer which can be obtained is a mixture of a polymer in which n differs, and the degree of many quantification is expressed with averaged n. Desirable n is 2-10 and especially 2-8 are preferred. Since it becomes become large too much and difficult to prepare the viscosity a hardenability

constituent, a large thing does not have preferred n.

[0037]As R, low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, and a butyl group, are illustrated among a general formula. A polymer of a tetraethoxysilane whose polymer of a tetramethoxy silane or R whose R is a methyl group is an ethyl group from fields, such as the hydrolysis nature of an alkoxy group and condensation nature, is preferred. Two or more R may differ in one molecule.

[0038]As a commercial polymer (B), Mitsubishi Chemical 51 [MKC silicate MS], MS56, MSEP2, the col coat methylsilicate 51, the ethyl silicate 40 and 40T, 48, N103X, HAS-10, Matsumoto Trading Olga Chicks SI series, the ethyl silicate 40 made from the Tama chemicals, and 45 grades are mentioned. [0039]In order to make high the degree of condensation of a polyfunctional hydrolytic silane compound to a polymer (B), organic acid, such as lactic acid and chloride, and inorganic acid can also be added to a polyfunctional hydrolytic silane compound. Therefore, a polymer (B) may contain a small amount of such acid.

[0040]In order to make a hardenability constituent of this invention promote hardening by humidity, a hardening accelerator catalyst which promotes a hardening reaction of reactive silyl groups may be used for it. As a hardening accelerator catalyst, an alkyl titanate, an organic silicon titanate, Amine salt, such as carboxylate, such as bismuth tris-2-ethylhexanoate, tin octylate, and dibutyltin dilaurate, and dibutyl amine 2-ethylhexanoate, other acid catalysts, and a basic catalyst can be used. [0041]A dehydrator may be added in order to improve storage stability further to a hardenability constituent of this invention. As a dehydrator, hydrolytic organicity silicone compounds, such as ORUTOGI acid alkyls, vinyltrimethoxysilane, and a tetraethoxysilane, a hydrolytic organic titanium compound, etc. can be used.

[0042]If still more nearly required for a hardenability constituent of this invention, a bulking agent, a plasticizer, etc. may be contained. As a bulking agent, can use a publicly known bulking agent, and specifically, Fumes silica, sedimentation nature silica, a silicic acid anhydride, hydrous silicic acids, and a bulking agent like carbon black, Fibrous fillers, such as bulking agents, such as calcium carbonate, diatomite, calcination clay, clay, talc, titanium oxide, bentonite, organic bentonite, ferric oxide, a zinc oxide, an active white, hydrogenation castor oil, and glass balloons, asbestos, glass fiber, and a filament, can be used.

[0043]As a plasticizer, can use a publicly known plasticizer and specifically Diethyl phthalate, Phthalic ester, such as phthalic acid benzyl ester, adipic acid octyl, Aliphatic-carboxylic-acid ester, such as succinic acid isodecyl, dibutyl sebacate, and butyl oleate, Epoxy plasticizers, such as phosphoric ester, such as glycol ester, such as pentaerythritol ester, and triresyl phosphate, epoxidized soybean oil, and epoxy stearic acid benzyl, a chlorinated paraffin, etc. can be independent, or can use it with two or more sorts of mixtures.

[0044]A hardenability constituent of this invention may contain still more publicly known various additive agents etc. As an additive agent, adhesive grant agents, such as epoxysilane, an mercaptosilane, and an epoxy resin, paints, various antiaging agents, an ultraviolet ray absorbent, etc. can be used.

[0045]By containing a polymer (B), hydrophilic nature of a hardenability constituent of this invention is improving, therefore compatibility of the surface of a hardened material which this hardenability constituent hardens with rain is improving. Therefore, when it rains, a flow side of surface rain becomes uniform, it can be begun by rain to pour dust, and it is thought that a sex with dust is mitigable.

[0046]This invention is a sealing agent which consists of the above-mentioned hardenability constituent again. Since a hardenability constituent of this invention is hardened under hygroscopic-surface-moisture existence at a room temperature and serves as a rubber elastomer, it is preferred to use it especially as an elastic sealing agent. When it is used as a sealing agent, it has the advantage that the hardened material surface which this constituent hardens has a high effect of mitigation of a sex with dust, and antifouling property is high.

[0047]This invention is a coating obtained by having applied the above-mentioned hardenability constituent to a substrate, and having stiffened it again. Since a coating obtained by having applied a hardenability constituent of this invention to a substrate, and having stiffened it has a high effect of mitigation of a sex with dust and its antifouling property is high, it can aim at reduction of a maintenance. Therefore, antifouling property of a substrate can be planned by covering a

hardenable constituent of this invention on the surface of a substrate for which especially antifouling property is needed, and considering it as a coating. As a substrate, a hardened material etc. which harden sealing agents other than a metal plate, a board made of a synthetic resin, a sheet, and a hardenable constituent of this invention are mentioned.

[0048] [Example] Hereafter, although an example (Examples 1-5, Examples 8-11) and a comparative example (Examples 6-7, Examples 12-13) explain this invention concretely, this invention is not limited to these.

[0049] [Example 1 of manufacture] Propylene oxide was polymerized with the zinchexacyano cobaltate catalyst by having used the diethylene glycol propylene oxide addition of the molecular weight 1000 as the initiator, and polyoxypropylene diol of the average molecular weight 10000 was obtained. Isooctate propylmethyl dimethoxysilane was added to this, the urethane-ized reaction was performed, the hydroxyl group of both ends was changed into the methyl dimethoxy silyl group, and the organic polymer (P1) which has an average of 1.2 reactive silyl groups per molecule was obtained.

[0050] [Example 2 of manufacture] Propylene oxide was polymerized with the zinchexacyano cobaltate catalyst by having used the diethylene glycol propylene oxide addition of the molecular weight 1000 as the initiator, and polyoxypropylene diol of the average molecular weight 17000 was obtained. After adding the methanol solution of sodium methylate to this and removing methanol, the allyl chloride was added and terminal hydroxyl groups was changed into the allyloxy group.

Furthermore, the addition reaction of the methyl dimethoxysilane was carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P2) which has an average of 1.6 reactive silyl groups per molecule was obtained.

[0051] [Example 3 of manufacture] Propylene oxide was polymerized with the zinchexacyano cobaltate catalyst by having used the glycerin propylene oxide addition of the molecular weight 1000 as the initiator, and polyoxypropylene triol of the average molecular weight 15000 was obtained. After adding the methanol solution of sodium methylate to this and removing methanol, the allyl chloride was added and terminal hydroxyl groups was changed into the allyloxy group. Furthermore, the addition reaction of the methyl dimethoxysilane was carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P3) which has an average of 1.8 reactive silyl groups per molecule was obtained.

[0052] [Example 4 of manufacture] After mixing powder caustic alkali of sodium to polyoxypropylene diol of the average molecular weight 4000, made it react to bromochloromethane, it was made to react to an allyl chloride further, and terminal hydroxyl groups was used as the allyloxy group. Furthermore, the addition reaction of the methyl dimethoxysilane was carried out by having made chloroplatinic acid into the catalyst, and the organic polymer (P4) was obtained. The average molecular weight of polyoxypropylene diol conversion of this organic polymer was 11000.

[0053] [Example 5 of manufacture] The tetraethoxysilane was hydrolyzed and the silane compound (B1) of the average molecular weight 744 which is a polymer of a tetraethoxysilane was obtained. [0054] [Example 6 of manufacture] The tetramethoxy silane was hydrolyzed and the silane compound (B-2) of the average molecular weight 390 which is a polymer of a tetramethoxy silane was obtained. [0055] [Examples 1-7] As opposed to 100 copies (it is [a weight section and the following] the same) of the organic polymers P1-P4, 50 copies of dioctyl phthalate, 120 copies of calcium carbonate, ten copies of titanium oxide, Three copies of hydrogenation castor oil, three copies of vinyltrimethoxysilane, one copy of phenolic antioxidant, The silane compound B1 or B-2 shown in two copies of aminosilanes and a table was kneaded as five copies and a curing catalyst for silicon resin under the conditions into which hygroscopic surface moisture does not go two copies of dibutyltin dilaurate, and the hardenable constituent was obtained (Examples 1-5).

[0056] The silane compound B1 - B-2 were not blended, and also the hardenable constituent was obtained similarly (Example 6). Furthermore instead of the silane compound B1 - B-2, the hardenable constituent which added five copies of tetraethoxysilanes (silane compound (B3)) was obtained (Example 7).

[0057] By exposing to humidity, these constituents started hardening promptly and changed to the good rubber elastomer. The result of having evaluated the surface contamination nature three months after exposing a presentation and hardened material of each hardenable constituent to the

outdoors is shown in Table 1. Evaluation of surface contamination nature made O fitness, and made x poor.

[0058] [Examples 8-13] When the hardenable constituent obtained in Example 2 and Example 4 was applied to the substrate shown in Table 2 by a thickness of 2 mm and having been exposed to humidity, hardening was started promptly and the hardened material obtained the coating firmly pasted up on the base material surface. The result of having evaluated the surface contamination nature three months after exposing this coating to the outdoors further is shown in Table 2.

Examples 12-13 look at the surface contamination nature of substrate I and RO which is not covered with a hardenable constituent for comparison. Substrate I shows an aluminum plate and substrate RO shows a poly chloridation vinyl sheet. Evaluation of surface contamination nature is the same as that of the above.

[0059]

[Table 1]

| 例 | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|--------|-----|-----|-----|-----|-----|-----|-----|
| 有機重合体 | P 1 | P 2 | P 3 | P 4 | P 2 | P 2 | P 2 |
| シラン化合物 | B 1 | B 1 | B 1 | B 1 | B 2 | - | B 3 |
| 表面汚染性 | ○ | ○ | ○ | ○ | ○ | × | × |

[0060]

[Table 2]

| 例 | 8 | 9 | 10 | 11 | 12 | 13 |
|--------|-----|-----|-----|-----|----|----|
| 硬化性組成物 | 例 2 | 例 2 | 例 4 | 例 4 | - | - |
| 基材 | イ | ロ | イ | ロ | イ | ロ |
| 表面汚染性 | ○ | ○ | ○ | ○ | × | × |

[0061]

[Effect of the invention] Preventable contamination nature of the surface of the coating obtained by having applied to the substrate the hardened material and hardenable constituent of this invention which harden a hardenable constituent, and having stiffened them is improving extremely.

[Translation done.]